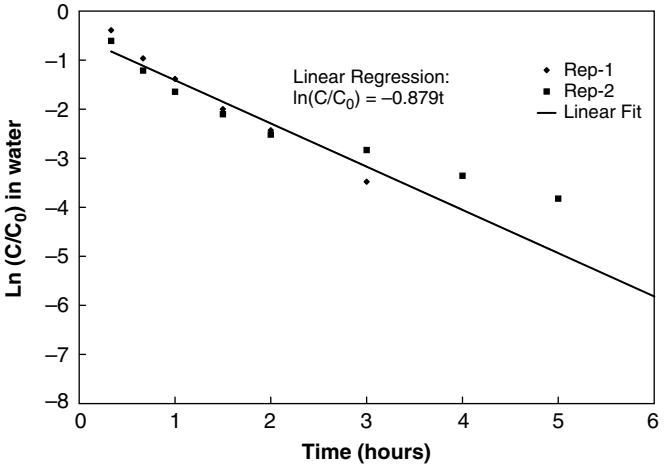

Figure 4-3. Linear transformation of data to obtain the depletion rate constant (Dr).

2.15×10^{-4} atm·m^3/mol, which is in good agreement with literature values (2.19×10^{-4} to 5.48×10^{-4}).

ACKNOWLEDGMENT

I would like to thank Josh Wnuk (Whitman College, Class of 2003) for data collection and analysis.

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IN THE LABORATORY

During the first laboratory period, you will prepare your purge apparatus (Sherer impinger) and during the following 24 hours take samples to determine the Henry's law constant for selected pesticides and PCBs. Your samples (Tenax resin tubes) can be extracted as you take them or during the beginning of the next laboratory period. In the second laboratory period you will analyze the sample extracts on the gas chromatograph and process your data.

Safety Precautions

- Safety glasses must be worn at all times during this laboratory experiment.
- Most if not all of the compounds you will use are carcinogens. Your instructor will prepare the aqueous solution of these compounds so that you will not be handling high concentrations. The purge solution you will be given contains parts per billion (ppb)-level concentrations and is relatively safe to work with. You should still use caution when using these solutions since the pesticides and PCBs are very volatile when placed in water. Avoid breathing the vapors from this solution.
- Extracts of the Tenax tubes should be conducted in the hood since you will be using acetone and isooctane, two highly flammable liquids.

Chemicals and Solutions

Neat solutions of the following compounds will be used by your instructor to prepare your aqueous solution:

- 2,2′-Dichlorobiphenyl
- Lindane
- 4,4′-Dichlorobiphenyl
- 2,2′,6,6′-Tetrachlorobiphenyl
- Aldrin
- 2,2′,4,4′,6,6′-Hexachlorobiphenyl
- 3,3′,4,4′-Tetrachlorobiphenyl
- Dieldrin
- 4,4′-DDD (dichlorodiphenyldichloroethane)
- 4,4′-DDT (dichlorodiphenyltrichloroethane)
- Methoxychlor
- Endosulfan I (not added to purge system, but used as a GC internal standard)

You will need, in addition:

- Tenax resin, chromatography grade
- Deionized water

Equipment and Glassware

- Sherer impingers (one per student group) (available from Ace Glassware; use the frit that allows gas to exit at the bottom of the impinger)
- Pasteur pipets filled with Tenax resin
- ~15-mL glass vials equipped with a Teflon-lined septum (12 per Sherer impinger setup or student group)
- Tygon tubing
- Brass or stainless steel fine metering valves
- Brass or stainless steel tees

PROCEDURE

In the lab, the Sherer impinger will already be set up and the purge solutions prepared. Your instructor will go over the setup and show its proper operation (Figure 4-4). Before you start the experiment, you will need to prepare Tenax resin sampling tubes. Tenax is a resin that has a high affinity for hydrophobic compounds and will absorb them when water or gas containing analytes is passed through the resin. Prepare the tubes by taking a glass Pasteur pipet and filling the narrow end with a small amount of glass wool. Next, place the Tenax resin tube in the pipet, leaving enough room for more glass wool at the constriction. This will leave about 1 to 2 cm of empty space at the top of the pipet (we will need this to add solvent to the pipet to desorb the analytes later). Clean the Tenax resin traps by passing at least 5 mL of pesticide-grade acetone through it, followed by 5 mL of pesticide-grade isooctane. Dry the tubes by placing them in the gas stream of the Sherer impinger (with no analyte present). You will need 14 tubes per Sherer impinger unless you desorb the tubes as you collect them.

If this is the case, you need only two tubes but you must still dry the tubes between samples. Tenax resin tubes should be wrapped and stored in aluminum foil.

1. Set up the impinger as shown by your instructor and set the gas flow rate while the flask is filled with deionized water (no analyte solution) (this will be a good time to purge the solvent from the Tenax purge tubes). Leave the final tube on the setup.
2. Leave the gas flow set as adjusted in step 1, but disassemble the apparatus and empty the flask.

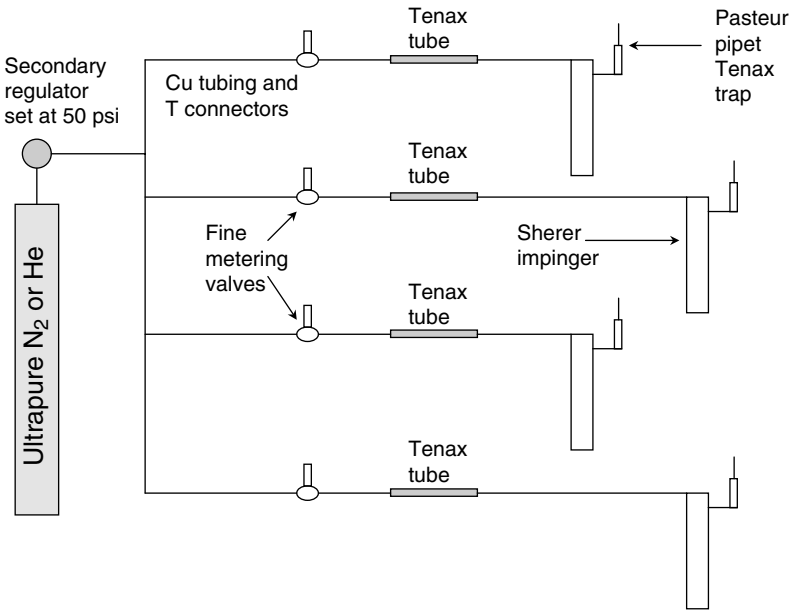

Figure 4-4. Multiple Sherer impinger setup.

3. Fill the flask with 300 mL of analyte-containing water.
4. Have a stopwatch or clock ready, assemble the Sherer flask, turn the ground-glass joint tightly to ensure a seal, and note the time. This is $t = 0$.
5. Check the flow rate and if needed, adjust it to 0.500 L/min.
6. Sample at the following times to obtain a complete purge profile:

   20 minutes
   40 minutes
   1.00 hour
   1.50 hours
   2.00 hours
   3.00 hours
   4.00 hours
   5.00 hours
   7.00 hours
   17.0 hours
   29.0 hours

Desorbing the Tenax Resin Tubes

7. Place the Tenax resin tube in a small clamp attached to a ring stand. Lower the tube so that it just fits into a ~15-mL glass vial.
8. Pipet 5.00 mL of pesticide-grade acetone onto the top of the Tenax resin trap. Allow the acetone to reach the top of the resin with gravity. You may have to apply pressure with a pipet bulb to break the pressure lock caused by bubbles in the tube, but be careful not to blow more air into the tube. After the second or third application (with a bulb) the acetone should flow with gravity. (The reason for adding acetone is to remove any water from the resin tube that will not mix or be removed by the hydrophobic isooctane.)
9. Pipet 5.00 mL of pesticide-grade isooctane onto the resin trap. After the isooctane has passed through the resin trap, force the remainder of the isooctane out of the pipet with a bulb. Remove the vial from below the tube, being careful not to spill any of the contents.
10. Add 10.0 mL of deionized water to the extraction vial and 0.25 g of NaCl. (NaCl will break any emulsion that forms in the solvent extraction step.)
11. Add 8.0 μL of a 32.70-ppm Endosulfan I (in isooctane) that your instructor will have prepared for you. Endosulfan I will act as an internal standard for the gas chromatographic (GC) analysis.
12. Seal the vial and shake it vigorously for 30 seconds. Allow the layers to separate, transfer 1 to 2 mL of the top (isooctane) layer into a autoinjection vial, and seal it.

13. Add your name to the GC logbook and analyze the samples using the following GC conditions:

    1.0-μL injection

    Inlet temperature = 270°C

    Column:

    HP-1 (cross-linked methyl silicone gum)
    30.0 m (length) by 530 μm (diameter) by 2.65 μm (film thickness)
    4.02-psi column backpressure
    3.0-mL/min He flow
    31-cm/s average linear velocity

    Oven:

    Hold at 180°C for 1.0 minute
    Ramp at 5.0°C/min
    Hold at 265°C for 16.0 minutes
    Total time = 34.0 minutes

    Detector:

    Electron-capture detector
    Temperature = 275°C
    Makeup gas = Ar with 1 to 5% CH_4
    Total flow = 60 mL/min

    A sample chromatogram is shown in Figure 4-5. Calibration standards will be supplied by your instructor and will range in concentrations from 1.00 to 500 ppb. Approximate retention times for the given GC setting are as follows:

Analyte	Elution Time (min)	Analyte	Elution Time (min)
2,2′-DCB	9.63	Endosulfan I (IS)	19.75
Lindane	12.13	Dieldrin	20.95
4,4′-DCB	12.71	DDD	22.20
2,2′6,6′-TCB	13.82	DDT	24.72
Aldrin	16.86	Methoxychlor	28.33
2,2′,4,4′,6,6′-TCB	18.86		

14. Sign out of the GC logbook and note any problems you had with the instrument.
15. Analyze the data and calculate the HLC for all the compounds in your samples.

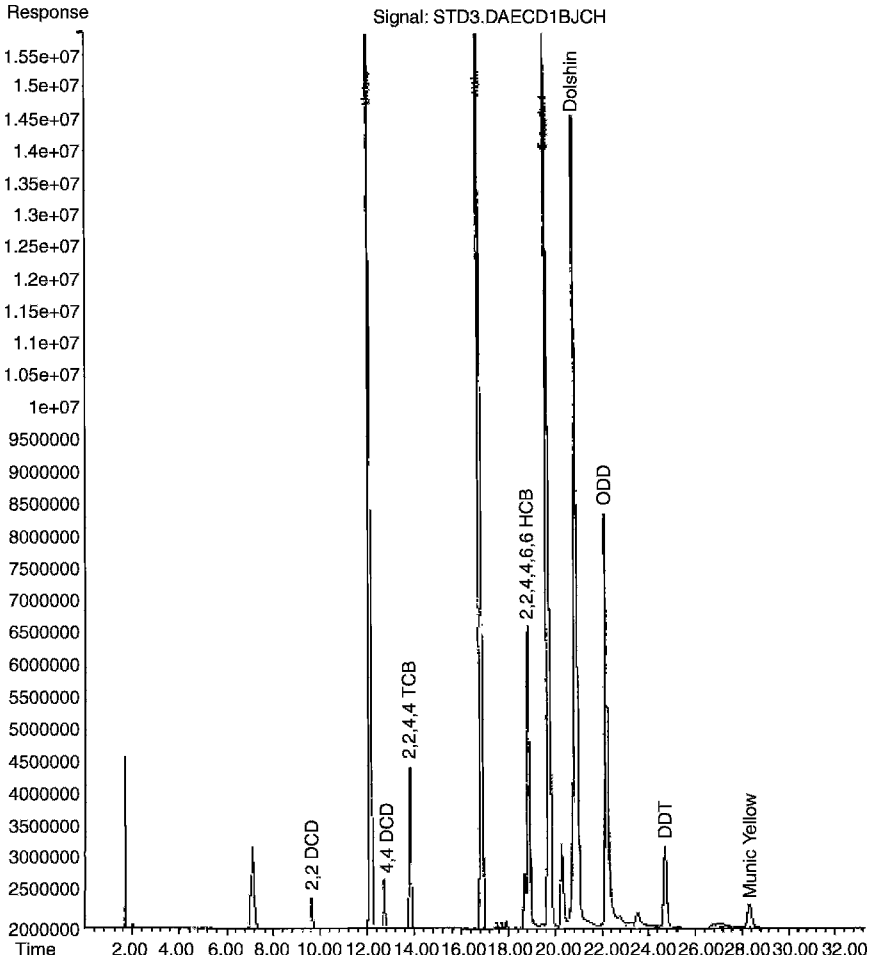

Figure 4-5. Output from the GC.

Waste Disposal

The water remaining in your Sherer impinger has been purged of all analytes and can be disposed of down the drain. Your sample extracts must be treated as hazardous waste since they contain acetone, isooctane, and chlorinated hydrocarbons. These should be placed in a glass storage container and disposed of in accordance with federal guidelines.

ASSIGNMENT

1. Turn in a diagram of your purge setup.
2. Turn in a spreadsheet showing the HLC calculation.
3. Compare the HLC values calculated to values from the literature.

ADVANCED STUDY ASSIGNMENT

1. Draw and describe each major component of a basic capillary column gas chromatograph.
2. Calculate the Henry's law constant with the data set in Table 4-2 for Dieldrin:

   Purge gas flow rate $= 0.500\,\mathrm{L/min}$
   System temperature $= 25^{\circ}\mathrm{C}$
   Total mass of Dieldrin in flask $(C_0) = 725\,\mathrm{ng}$
   Volume in Sherer impinger $= 300\,\mathrm{mL}$

   Mass in each purge interval is in measured in nanograms. Express your answer in $\mathrm{atm \cdot m^3/mol}$.
3. Compare your answer to the value from a reference text or a value from the Internet.

TABLE 4-2. Sample Data Set

Purge Interval Time (days)	Purge Interval Time (hrs)	Mass in Purge Interval R-1	Mass in Purge Interval R-2	Cummulative Mass in Purge Interval R-1	Cummulative Mass in Purge Interval R-2	C/Co R1	C/Co R2	ln (C/Co) R1	ln(C/Co) R2
0.01389		65.16	66.5						
0.02778		77.76	74.8						
0.04167		73	71.9						
0.0625		72.8	75.2						
0.08333		69.9	70						
0.125		86.9	84.5						
0.16667		80.7	69.8						
0.20833		76.1	61.6						
0.2917		77.5	63						

DATA COLLECTION SHEET

5

GLOBAL WARMING: DETERMINING IF A GAS IS INFRARED ACTIVE

Purpose: To learn to use an infrared spectrophotometer

To determine if a gas is infrared active

BACKGROUND

Although global warming has drawn growing political attention in recent decades, relatively few people understand its causes and implications. Global warming has two faces, one that benefits us and another that may cause serious environmental and economic damage to the planet. Conditions on Earth would be very different without the *greenhouse effect* of atmospheric warming. Natural atmospheric gases, including carbon dioxide and water vapor, are responsible for adjusting and warming our planet's atmosphere to more livable conditions. In fact, there is one popular theory that the Earth is actually a living organism and that under normal conditions (without human interference), the Earth will maintain the life-sustaining environment that it has acquired over the last 100 million years or so. This theory is the *Gaia hypothesis* proposed by James Lovelock, and there are several short books on the subject.

The bad side, the anthropogenic side, of global warming is still strongly debated between some politicians and scientists, but it is generally well accepted among scientists that humans are contributing exponentially to the warming of the planet. Unfortunately, some governments and political parties side with the

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economists, who often have little knowledge of the science behind the argument but are concerned primarily with constant economic growth rather than sustained growth. This bad side to global warming has been studied for several decades and data from these studies is presented below.

First, it is important to understand the nature of the light coming from our Sun to the Earth. Figure 5-1 shows three representations of the wavelengths and intensity of light coming from the surface of the Sun (at 5900 K). The upper dashed line represents the wavelengths and intensity of light as predicted by physicists for a blackbody residing at the temperature of the sun. This line predicts fairly accurately the spectrum of wavelengths observed just outside the Earth's atmosphere by satellites (represented by the upper solid line). The remaining line (the lower solid line) shows the spectrum of wavelengths detected at the Earth's sea surface using similar satellites. As you can see, some of the intensity is reduced and a few of the wavelengths are removed completely by atmospheric gases. The wavelengths in Figure 5-1 are given in micrometers, with ultraviolet (UV) radiation between 0 and 0.3 on the *x* axis, visible light from 0.3 to about 0.8 and near-infrared (IR) from about 0.8 to the far right side of the plot. As you see, most of the solar radiation entering Earth's atmosphere is in the form of visible light and near-IR radiation.

Next, notice the difference between the UV radiation intensity outside the atmosphere and at sea level. These wavelengths, which cause damage to skin and other materials, are removed in the stratosphere during the formation of ozone shown below (diatomic oxygen absorbs these wavelengths, splits into free oxygen

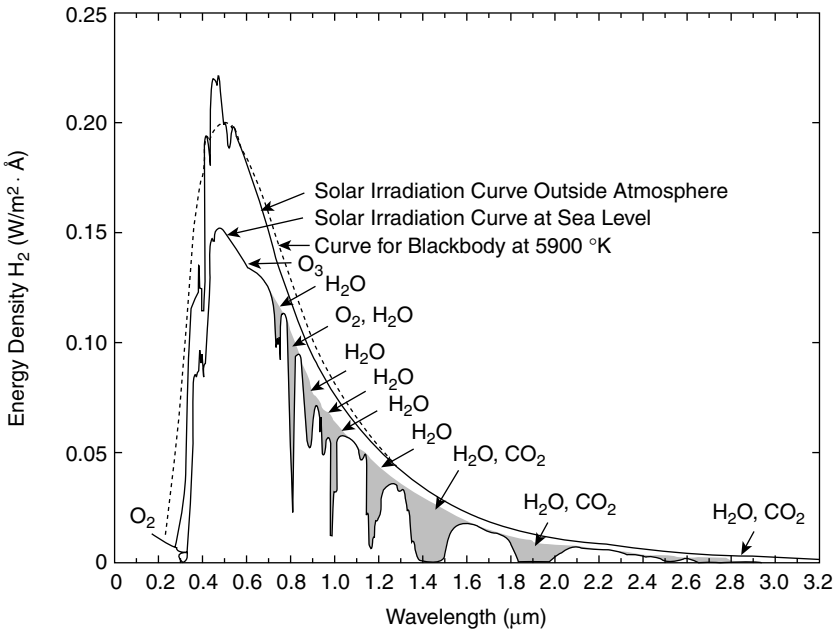


Figure 5-1. Wavelengths and intensity of wavelengths of radiation emitted by the sun and reaching Earth's sea surface. (From Department of the Air Force, 1964.)

radicals, and binds to another O_2 to form O_3). This is the source of concern with chlorofluorohydrocarbons, which interfere with this process and promote the destruction of O_3, thus allowing more high energy UV to reach Earth's surface.

$$O_2(g) + h\nu \rightarrow 2O_2(g)$$
$$O_2(g) + O_2(g) + M \rightarrow O_3(g) + M^*(g) + \text{heat}$$

Visible light is also attenuated significantly by Earth's atmosphere, but not to the extent that it limits the growth of plant life. Some of the visible light is simply absorbed and rereleased as heat in the atmosphere. Other visible wavelengths are scattered and reflected back into space, which is why the astronauts can see the Earth from space. Several compounds in the atmosphere partially or completely absorb wavelengths in the near-IR radiation on the left side of the figure. Absorption of these wavelengths is represented by the shaded areas for O_3, H_2O, O_2, and CO_2. This is one mechanism of global warming, in which the atmosphere is heated by IR radiation incoming from the Sun rather than reradiated from Earth's surface. To fully understand the importance of these gases in global warming, we must also look at the type of radiation the Earth is emitting.

As visible light reaches Earth's surface, it is absorbed by the surface and transformed into heat. This heat is reemitted back into the atmosphere and space by Earth. When physicists estimate the wavelengths and intensity of wavelengths for Earth as a blackbody at 320 K, the dashed-line spectrum shown in Figure 5-2 results. Note that the wavelengths released by Earth are much longer wavelength (far, far to the right of the wavelengths shown in Figure 5-1). These far-infrared

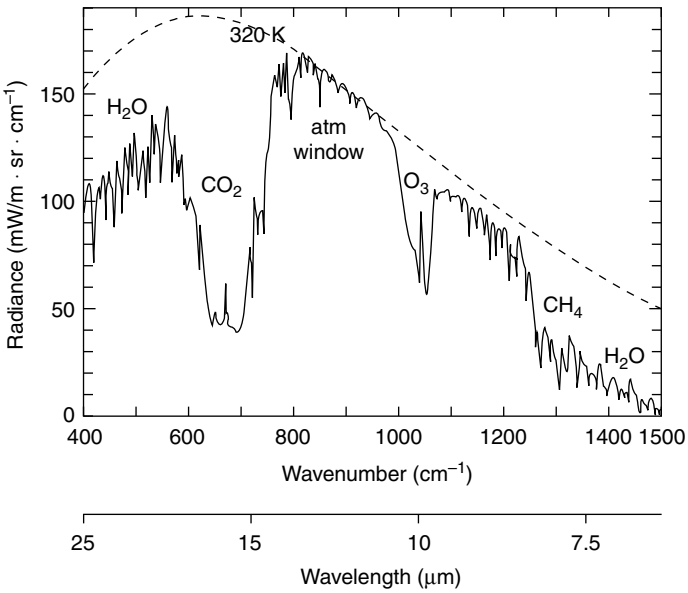


Figure 5-2. Wavelengths and intensity of wavelengths of radiation emitted by the Earth. (From Hanel et al., 1972.)

wavelengths are very susceptible to being absorbed by atmospheric gases, as indicated by the decrease in intensity shown by the solid line. The solid line shows the wavelength and intensity of wavelengths measured by a satellite above Earth's surface, but this time the satellite is pointed at Earth instead of the Sun. Note the strong absorbance by atmospheric constituents, primarily water, methane, and carbon dioxide. By absorbing the IR radiation instead of letting it pass freely into space, the gases heat Earth's atmosphere. The amount of global warming resulting from the reflected IR radiation is related directly to the concentration of atmospheric gases that can absorb the emitted IR radiation. Before we can evaluate the cause of the ''bad'' global warming, we must look at historical data on concentrations of greenhouse gases (IR-active gases) in the atmosphere.

In the 1950s the U.S. government initiated a project to collect baseline data on planet Earth. One of the most important studies was to monitor the concentration of CO_2 in a remote, ''clean'' environment. The site selected for this monitoring program was the observatory on Mauna Loa in Hawaii. This site was selected for its location in the middle of the Pacific, away from major pollution sources, and for its high altitude (about 14,000 feet). Data from this monitoring program are shown in Figure 5-3 and are available from the LDEO Climate Data Catalog, which is maintained by the International Research Institute at Columbia University (`http://www.ingrid.ldgo.columbia.edu/`). Data from 1958 to the year 2000 (not shown) consistently show an increase in atmospheric CO_2 concentrations. In addition, for the first time we can actually see the Earth ''breath,'' as indicated in the inset in Figure 5-3: In the summer, when plant growth is highest in the northern hemisphere, CO_2 levels are at a minimum. This is followed by fall, when plant growth is subsiding and dying, and CO_2 levels start to increase. The CO_2 concentration reaches a maximum in winter, followed by a decrease in spring as plants start growing again to repeat the cycle.

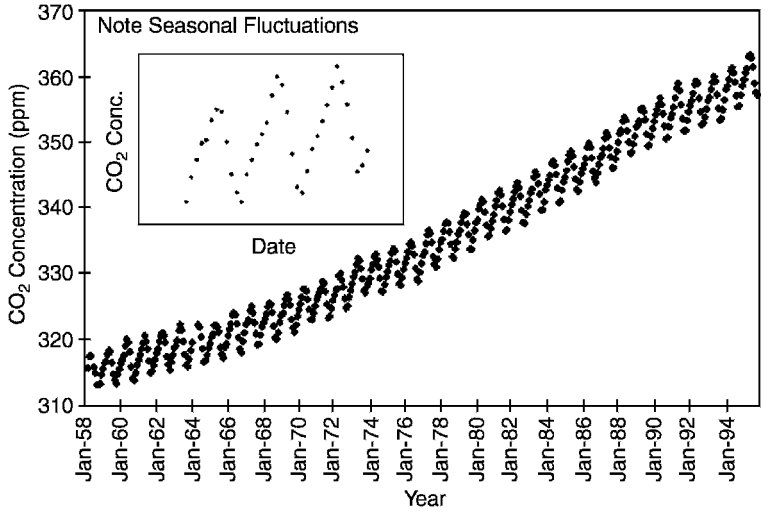


Figure 5-3. CO_2 measurements from Mauna Loa. (Data from `http://ingrid.ldgo.columbia.edu/.`)

One problem with the data set from Mauna Loa is that it represents only a small snapshot in time; with issues such as global warming, we must look at long-term geological time scales. To do this, scientists have collected ice cores from a variety of places across the Earth. Ice cores represent a long history of atmospheric data. As snow falls over cold areas and accumulates as snow packs and glaciers, it encapsulates tiny amounts of atmospheric gases with it. When ice cores are taken and analyzed carefully, they can give information on the composition of the atmosphere at the time the snow fell on the Earth. An example of these data for the Vostok ice core is shown in Figure 5-4. This data set goes back in time 160,000 years (from left to right) from the present and gives us a long-term idea of the composition of the atmosphere. The three figures show the concentration of CH_4 with time (Fig. 5.4*a*), the concentration of CO_2 with time (Fig. 5.4*b*), and the estimated temperature with time (Fig. 5.4*c*). The CH_4 and CO_2 data are self-explanatory and are simply the gases trapped in the glacier, but the temperature data are a bit more complicated. To estimate the temperature as a function of time, scientists look at the abundance of the oxygen-18 isotope in glacial water. Water on Earth contains mostly oxygen-16, but a small amount of oxygen-18 is present. During warmer geologic times on Earth, more water containing ^{18}O is evaporated from the oceans and falls as snow over cold regions. In contrast, cooler geologic times will have less ^{18}O in the atmospheric and snow. By conducting experiments we can estimate how much ^{18}O is present at a given temperature and estimate what the temperature was when each layer of the glacial water was deposited. This allows Figure 5-4*c* to be created. When the three figures are compared, a strong correlation between high CH_4 concentrations, high CO_2 concentrations, and high temperature is noticed. This can be understood by

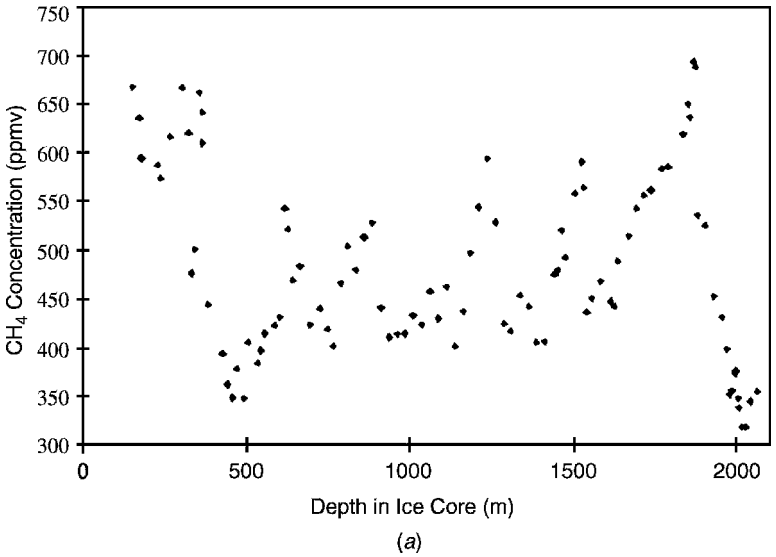
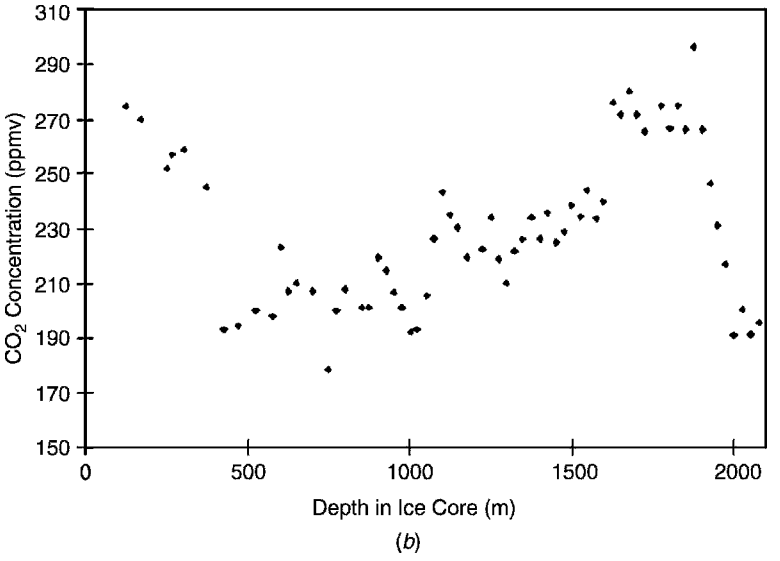


Figure 5-4. (*a*) CH_4, (*b*) CO_2, and (*c*) temperature data from the Vostok ice core study. (Data from `http://ingrid.ldgo.columbia.edu/.`)



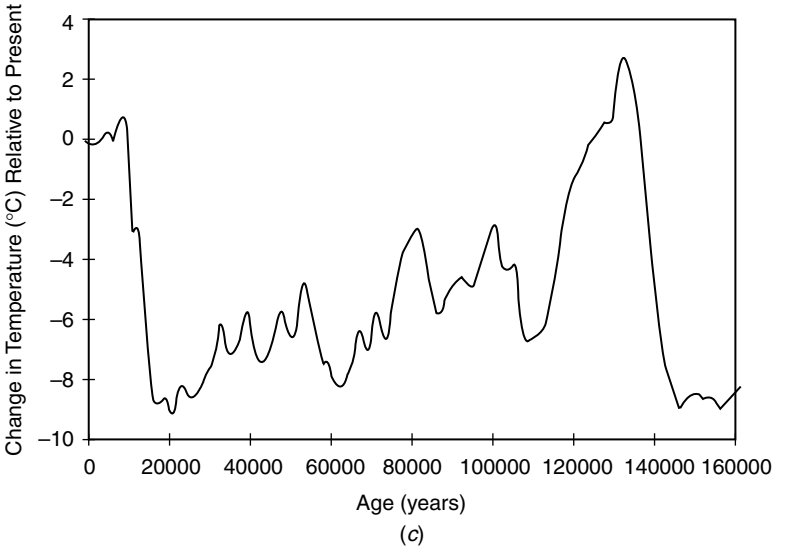


Figure 5-4. (*Continued*)

returning to Figures 5-1 and 5-2 and noting which gases absorb or trap energy in Earth's atmosphere.

Now we combine the CO_2 data from the Vostok ice core and the Mauna Loa data set to create Figure 5-5. Note in the figure that the direction of time changes, going back in time from left to right. This figure contains data going back 160,000 years, and we notice two distinct spikes in CO_2 concentration (and in temperature if we look again at Figure 5-4). The important point to note in Figure 5-5 is the rate at which the CO_2 (and temperature) has changed over time. The natural

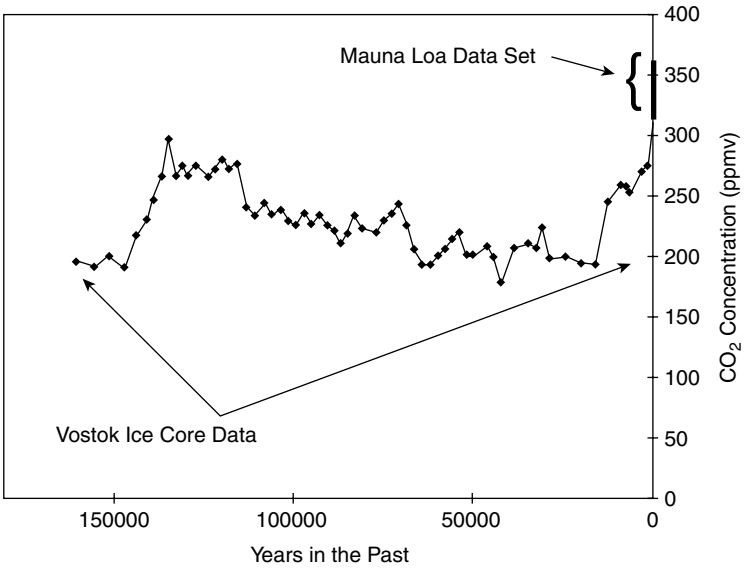


Figure 5-5. Combined data from the Vostok ice core and the Mauna Loa studies. Note the rapid change in CO_2 levels during the present time. The Mauna Loa data are from Keeling (1995, 1996); the Vostok ice core data are from Barnola et al. (1987), Genthon et al. (1987), and Jouzel et al. (1987). (Data from `http://ingrid.ldgo.columbia.edu/.`)

change in CO_2 around 130,000 years ago took more than 30,000 years to go from the lowest to the highest concentration. Similarly, the recent climb in temperature took approximately 20,000 years to reach its current level. This is in contrast to the drastic rate of change that is present in the Mauna Loa data set. This 50-ppm change in CO_2 concentration has occurred in only 50 years, and most predictions of future atmospheric CO_2 concentrations (if we continue to consume petroleum products at current rates) are in the range 700 to 800 ppm by the year 2100 (locate this point in Figure 5-5). This is the global warming that concerns us directly. Some people call for more study of the problem and wish to maintain our use of fossil fuels to preserve our economic status, but based on the data presented here, this is one experiment that we may not wish to conduct.

Although many scientists accept that global temperatures are rising, they are less in agreement about the effects of global warming, Most, however, agree on the following predictions:

- Warmer temperatures (averaging 5 to 10°C by the year 2100)
- Loss of coastal areas to flooding
- Damage to coral reefs (bleaching)
- Increased incidence of violent weather
- Increased outbreaks of diseases (new and old)
- Changing regional climates (wetter or drier, depending on where you live)

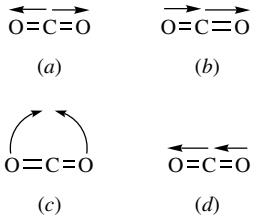


Figure 5-6. Vibrational structures for CO_2.

THEORY

In the background section we saw which greenhouse gases absorb IR radiation and at what wavelengths. But what actually makes a gas IR active? There are two prerequisites for a gas to be IR active. First, the gas must have a permanent or temporary dipole. Second, the vibration of the portion of the molecule having the dipole must be at the same frequency as the IR radiation that is absorbed. When these two criteria are met, the gas molecule will absorb the radiation, increase its molecular vibrations, and thus retain the heat in the atmosphere. This is why gases such as O_2 and N_2 are not IR active; they do not have permanent or sufficiently temporary dipoles. Molecules such as chlorofluorocarbons (CFCs), on the other hand, have permanent dipoles and are very IR active (actually, this is the *only* connection between global warming and ozone depletion—CFCs are active in both cases). However, what about symmetrical molecules such as CO_2 and CH_4? To understand how these molecules are IR active, we must draw their molecular structures.

Figure 5-6 shows several possible vibrational structures for CO_2. The arrows indicate the direction of the stretch. Figure 5-6*a* is the normal way we think about CO_2, with each carbon–oxygen bond stretching in unison and away from the central carbon atom and no dipole present in the molecule. However, the stretches in Figure 5-6*b*, *c*, and *d* are also possible and result in a temporary dipole that can absorb IR radiation. Similar observations can be made for methane (Figure 5-7). The symmetrical orientation is shown in Figure 5-7*a*, while asymmetrical molecules are shown in Figure 5-6*b* and *c*, which contain temporary dipoles. The latter two molecules absorb IR radiation and result in a heating of the atmosphere.

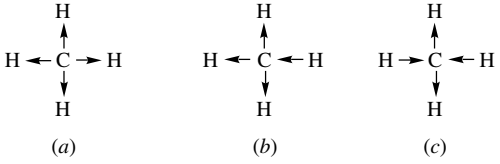


Figure 5-7. Molecular vibrations for methane.

ACKNOWLEDGMENT

I would like to thank Dr. Paul Buckley for taking the IR readings given in the instructor's version of this manual.

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IN THE LABORATORY

There is no exact procedure for conducting this laboratory other than consulting the users' guide for your IR instrument. Sign in the instrument logbook and remember to record any problems with the instrument when you finish. You will be provided with a variety of gases that you will measure on your IR instrument. Print out the spectrum for each gas and use the resources in your library to determine what type of vibration is occurring at each wave number where you observe absorption of IR radiation.

Safety Precautions

- Avoid the use of methane or other flammable gases around electronic equipment or flames.

Chemicals

- *Gases*: N_2, O_2, a CFC, a CFC substitute, CO_2, and CH_4

Equipment

- IR spectrophotometer
- IR gas cell

Waste Disposal

The gas cells should be filled and emptied in a fume hood.

ASSIGNMENT

Turn in your IR spectrum and label each peak with respect to the vibration that is occurring.

ADVANCED STUDY ASSIGNMENT

1. What are the requirements for a gas to be IR active?
2. Look up the composition of Earth's atmosphere. Which gases would you expect to be IR active?
3. Draw a diagram of a basic IR instrument and explain how it works.
4. Using the Internet, find how much CO_2 is emitted each year by the most productive nations. Which nation has the largest emissions?

6

MONITORING THE PRESENCE OF HYDROCARBONS IN AIR AROUND GASOLINE STATIONS

Purpose: To determine the exposure of citizens to gasoline vapors

To learn to use a personal sampling pump

To learn to analyze gasoline components on a gas chromatograph

BACKGROUND

Each day we are exposed to a variety of organic vapors. Yet we experience perhaps the greatest level of exposure when we fill our automobiles with gasoline. Gasoline contains a variety of alkanes, alkenes, and aromatics. In California alone, it has been estimated that 6,100,000 lb of gasoline vapors per year are released into the atmosphere (`http://www.arb.ca.gov`). It is also interesting to note that at least 23 of the 1430 National Priorities List sites (compiled by the U.S. Environmental Protection Agency) contain automotive gasoline (`http://www.atsdr.cdc.gov`).

Table 6-1 shows the approximate composition of unleaded gasoline. You should note several carcinogens in this list. The right-hand column shows data on exposure limits (`http://www.bpdirect.com`); the allowed concentrations shown are relatively high compared to some pollutant exposures, but if you consider how often you (or the gas station attendant) are exposed to these vapors, you may start to appreciate the problem and potential cancer risk.

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TABLE 6-1. Composition of Unleaded Gasoline

Component	Percent Range by Weight	Exposure Limits (ppm)
Benzene	0–3	1–5
Butane	4–6	800
Cyclohexane	0–1	300
Ethylbenzene	0–2	100–125
Heptane	6–8	400–500
Hexane	6–8	50–500
Pentane	9–11	600–1000
Toluene	10–12	100–200
Trimethylbenzene	0–3	25
Xylene	8–10	100

Source: `http://www.bpdirect.com`

But what exactly are the risks of exposure? Laboratory animals (rats and mice) exposed to high concentrations of gasoline vapors (at 67,262 and 2056 ppm) showed kidney damage and cancer of the liver. *n*-Heptane and cyclohexane can cause narcosis and irritation of the eyes and mucous membranes. In studies using rabbits, cyclohexane caused liver and kidney changes. Benzene, a known human carcinogen, has an eight-hour exposure limit of 0.5 ppm. Studies have shown that exposure to benzene vapor induce leukemia at concentrations as low as 1 ppm. Trimethylbenzene (isooctane) has an eight-hour exposure limit of 25 ppm and above this limit can cause nervousness, tension, and anxiety as well as asthmatic bronchitis. *n*-Hexane has been shown to cause peripheral nerve damage and hexanes show narcotic effects at 1000 ppm. Toluene can cause impairment of coordination and momentary memory loss at 200 to 500 ppm. Palpations, extreme weakness, and pronounced loss of coordination can occur at 500 to 1500 ppm. The eight-hour exposure limit for toluene is 100 ppm. (Data in this paragraph were obtained from `http://www.brownoil.com.`)

As you can see from the discussion above, exposure to gasoline vapors, although routine, should be of concern to anyone filling his or her automobile's gas tank.

THEORY

The sampling of gasoline vapors is a relatively easy process. Figure 6-1 shows a typical sampling pump and sample cartridge. The pump comes calibrated from the factory with respect to airflow, and the flow can be adjusted on most pumps. The pump pulls the air and vapors through the sampling tube, thus avoiding both contamination of the sample tube with compounds from the pump and contamination of the sampling pump with gasoline vapors. A variety of sample tubes are available, with difference resins designed for efficient adsorbance of analytes of

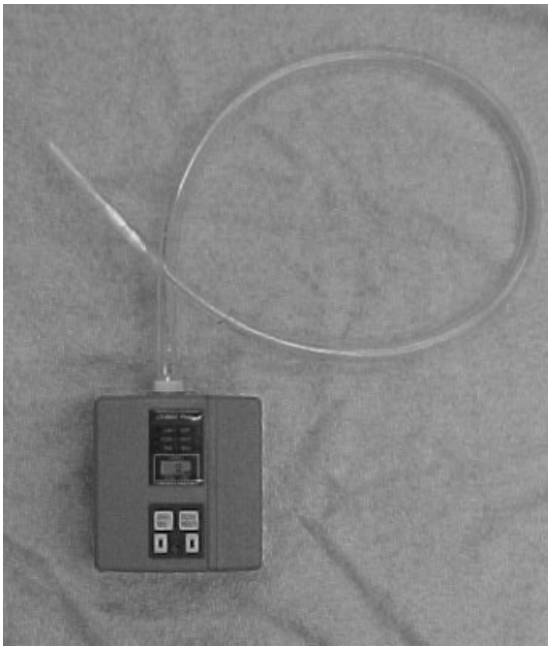

Figure 6-1. Q-Max personal sampling pump. (Supelco, Inc.)

interest. The tube you will use is filled with fine-grained charcoal. Each tube contains two compartments of resin. The large compartment is at the end where the vapors are drawn into the system. The air then passes through a smaller compartment, which is analyzed separately to see whether vapors have saturated the first compartment of resin and passed to the second compartment. When this saturation occurs, it is referred to as breakthrough, and the sample is not usable, since you do not know if vapor has also passed the second tube. The only difficult task in designing a sampling procedure is to determine how long to sample to trap enough vapors to analyze on the gas chromatograph. Your instructor will specify how long you should sample but typically a 5 to 10 minute sample will suffice. You will also be using decane as an internal standard for the GC. Your instructor will review the use of this approach at the beginning of the laboratory.

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IN THE LABORATORY

You will be divided into groups and sent to a local gasoline station to take samples. Your instructor will have already contacted the owner of the station and asked for permission. You may actually fill cars with gasoline, or you may simply stand beside car owners (or station attendants) as they operate the pumps. Next, you will extract the samples and analyze them on the GC. There are many compounds present in gasoline, but we will only be analyzing selected compounds.

Safety Precautions

- Safety glasses must be worn when in the laboratory.
- All of these vapors have exposure limits, and many are carcinogens. Avoid exposure to these vapors in the laboratory by working in fume hoods. Your instructor may choose to use carbon disulfide, a highly toxic and cancer-causing agent. *Always* work in the fume hood with this solvent, even when filling the syringe for injection into the GC.

Chemicals and Solutions

We will analyze for the compounds shown in Table 6-2. Decane will be used as the internal standard that will be added to your desorption (extraction) solvent (pentane or carbon disulfide) as well as the GC calibration standards at a concentration of 29.2 ppm. You will use the density to calculate the concentration in your calibration standards (volume added times density equals mass added to volumetric).

Use the data shown in Table 6-3 to prepare your GC calibration standards if these standards are not provided from the stockroom. The solvent used for your samples and standards will be pentane or carbon disulfide containing the same concentration of decane as used in the calibration standards. You will also need approximately 50 mL of internal standard solution for extraction of your samples from the charcoal. Your instructor may also have this solution prepared.

TABLE 6-2. Density of Compounds to Be Used in Calibration Standards

Compound	Density (g/mL or mg/mL)	Compound	Density (g/mL or mg/mL)
Benzene	0.8787	*m*-Xylene	0.8684
Ethyl benzene	0.866	*o*-Xylene	0.8801
n-Heptane	0.684		
Isooctane	0.6919	Decane	0.73 (internal standard)
Toluene	0.866		

TABLE 6-3. Solutions for Making Calibration Standards from Pure (Neat) Compounds[a]

Compound	μL Neat to a 25-mL Vol.	Mass (mg) in Vol.	Stock Conc. in 25-mL Vol.	Std. 1 1 : 50 Dilution, Then 1 : 10	Std. 2 1 : 50 Dilution Then 2 : 10	Std. 3 1 : 50 Dilution, Then 5 : 10	Std. 4 1 : 50 Dilution	Std. 5 1 : 25 Dilution
Benzene	50	43.935	1757.4 ppm	3.5148	7.0296	17.574	35.148	70.296
Ethyl Benzene	50	43.3	1732	3.464	6.928	17.32	34.64	69.28
n-Heptane	50	34.2	1368	2.736	5.472	13.68	27.36	54.72
Isooctane	50	34.595	1383.8	2.7676	5.5352	13.838	27.676	55.352
Toluene	50	43.3	1732	3.464	6.928	17.32	34.64	69.28
m-Xylene	50	43.42	1736.8	3.4736	6.9472	17.368	34.736	69.472
o-Xylene	50	44.005	1760.2	3.5204	7.0408	17.602	35.204	70.408
Decane	50	36.5	1460	29.2	29.2	29.2	29.2	29.2

[a] Use the densities shown in Table 6-2. Concentrations of analytes in standards 1–5 are in ppm. Note that the concentrations of Decane should be the same (29.2 ppm) in all standards and sample extracts.

TABLE 6-4. Approximate Retention Times for Analytes on a DB-1 Column

Analyte	Retention Time (min)	Analyte	Retention Time (min)
Benzene	4.52	Toluene	8.05
Ethyl Benzene	10.67	*m*-Xylene	10.88
n-Heptane	6.33	*o*-Xylene	11.43
Isooctane	5.95		

GC Conditions

- Splitless for the first 2 minutes, split mode for the reminder of the analysis
- Injector temperature: 250°C
- Detector temperature: 310°C
- Oven: Initial temp 40°C
  Hold for 5 minutes
  Ramp at 10°C/min to 200°C
  Hold for 5 minutes (or less)
- Column: DB-1 or DB-5
- Injection volume: 1 μL
- Integrator settings: Attenuation 3
  Threshold 3
- Retention times (Table 6-4)

Equipment and Glassware

- 10-mL Teflon-septum capped vials for extracting sample charcoal
- Needle-nosed pliers for breaking the sample containers
- Capillary column gas chromatograph
- 1-, 2-, and 5-mL volumetric pipets

PROCEDURE

Week 1

1. Your instructor will assign you times and dates to sample at a local gasoline filling station. Each group will take one sample. Use a piece of plastic tubing to position the sample point at shoulder level.
2. If you are using carbon disulfide as your extraction solvent, take a sample over a 5 to 10 minute period. It typically takes 0.75 to 1.5 minutes to fill an empty tank, so you will have to take a composite sample while filling several cars. Remember to turn the pump off between cars. If you are using pentane as your extraction solvent, you will need to sample for 10 minutes.
3. Cap the ends of the sampling tube with the caps included in your kit when you are finished.

Week 2

4. Start the GC, and run your calibration standards while you prepare your samples.
5. Extract (desorb) your sample tubes as illustrated by your laboratory instructor. You will need to place the charcoal from the front and back in two separate vials.
6. Add 1.00 mL of your extraction solvent containing decane (your internal standard).
7. Cap the vial and allow it to stand for 5 minutes.
8. Analyze each sample on the GC.

Waste Disposal

All extraction solvents, calibration standards, and liquid waste should be collected in an organic waste container and disposed of by your chemistry stockroom. Your sample tubes can be disposed of in the broken-glass container.

ASSIGNMENT

1. Calculate the concentration of each analyte in an extract and the total mass of each analyte in your extraction vial.
2. Use the flow rate and sample period to convert the total mass collected to the average concentration in the air ($\mu g/m^3$ or ng/m^3).
3. Does your dose exceed the limit mentioned in the background material?

ADVANCED STUDY ASSIGNMENT

1. Draw and label a basic capillary column gas chromatograph.
2. Describe each major component in one to three sentences.

DATA COLLECTION SHEET

PART 3

EXPERIMENTS FOR WATER SAMPLES

7

DETERMINATION OF AN ION BALANCE FOR A WATER SAMPLE

Purpose: To determine the ion balance of a water sample and learn to perform the associated calculations

To learn the use of flame atomic absorption spectroscopy unit

To learn the use of an ion chromatograph unit

BACKGROUND

A favorite cartoon from my childhood shows Bugs Bunny preparing water from two flasks, one containing H^+ ions and another containing OH^- ions. Although this is correct in theory, only Bugs could have a flask containing individual ions. In reality, counterions must be present. For example, in highly acidic solutions, the H^+ ions are in high concentration but must be balanced with base ions, usually chloride, nitrate, or sulfate. In high-pH solutions, the OH^- ions are balanced by cations such as Na^+, K^+, or Ca^{2+}. The combined charge balance of the anions and cations must add up to zero in every solution. This is the principle behind the laboratory exercise presented here. You will analyze a water solution for anions by ion chromatography (IC) and for cations by flame atomic absorption spectroscopy (FAAS) and use these data to determine the ion balance of your solution. Of course, this exercise is easier than in real life, where you would have no idea which ions are present and you would have to analyze for every possible cation and anion. In this exercise we tell you which anions and cations are present.

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The presence of a variety of cations and anions in solution is very important to organisms living in or consuming the water. For example, we could not live by drinking distilled or deionized water alone. We need many of the ions in water to maintain our blood pressure and the ion balance in our cells. This need for ions in solution is important even for microorganisms living in water, since water is their medium of life. In distilled water, microbial cells try to balance the ionic strength between the internal (cell) and external water. In doing so in distilled water, the microbe cell will expand and could rupture, due to the increased volume of water required to balance the osmotic pressure across the cell membrane.

Another important point concerning ionic strength is the toxicity of inorganic pollutants, specifically metals and nonmetals. In general, the predominant toxic form of inorganic pollutants is their hydrated free ion. However, notable exceptions to this rule include organic forms of mercury and the arsenic anion. Inorganic pollutants are also less toxic in high–ionic strength (high-ion-containing) waters, due to binding and association of the pollutant with counterions in solution. This is called *complexation* and is the focus of computer models such as Mineql, Mineql+, and Geochem. For example, consider the toxicity of the cadmium metal. The most toxic form is the Cd^{2+} ion, but when this ion is dissolved in water containing chloride, a significant portion of the cadmium will be present as $CdCl^{+}$, a much less toxic form of cadmium. Similar relationships occur when other anions are present to associate with the free metal.

THEORY

When the concentration of all ions in solution is known, it is relatively easy to calculate an ion balance. An example is shown in Table 7-1 for a river water

TABLE 7-1. Example Calculation of the Electroneutrality of a Hypothetical River Water Sample

Ion	Molar Concentration (mol/L)	Charge Balance	Total Ion Balance
Cations			
Ca^{2+}	3.8×10^{-4}	7.6×10^{-4}	
Mg^{2+}	3.4×10^{-4}	6.8×10^{-4}	
Na^{+}	2.7×10^{-4}	2.7×10^{-4}	
K^{+}	5.9×10^{-5}	5.9×10^{-5}	
			Total cations: 1.77×10^{-3}
Anions			
HCO_3^{-}	9.6×10^{-4}	9.6×10^{-4}	
Cl^{-}	2.2×10^{-4}	2.2×10^{-4}	
F^{-}	5.3×10^{-6}	5.3×10^{-6}	
SO_4^{2-}	1.2×10^{-4}	2.4×10^{-4}	
NO_3^{-}	3.4×10^{-4}	3.4×10^{-4}	
			Total anions: 1.77×10^{-3}
			Net difference: 0.00×10^{-3}

Source: Adapted from Baird (1995).

sample. In the data analysis for this laboratory report, you must first convert from mg/L to molar concentration. Cations and anions in Table 7-1 are separated into two columns, and each molar ion concentration is multiplied by the charge on the ion. For calcium, the molar concentration of 3.8×10^{-4} is multiplied by 2 because calcium has a $+2$ charge. The molar charges are summarized, and if all of the predominant ions have been accounted for, the difference between the cations and anions should be small, typically less than a few percent of the total concentration. A sample calculation is included in the Advanced Study Assignment. Note that an important step in going from your analyses to your final ion balance number is to account for all dilutions that you made in the lab.

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Dionex DX-300 Instrument Manual.

IN THE LABORATORY

Safety Precautions

- As in all laboratory exercises, safety glasses must be worn at all times.
- Use concentrated HNO_3 in the fume hood and avoid breathing its vapor. For contact, rinse your hands and/or flush your eyes for several minutes. Seek immediate medical advice for eye contact.

Glassware

- Standard laboratory glassware: class A volumetric flasks and pipets

Chemicals and Solutions

- ACS or reagent-grade NaCl, KCl, $MgSO_4$, $NaNO_3$, and $Ca(NO_3)_2$ (salts should be dried in an oven at 104°C and stored in a desiccator)
- 1% HNO_3 for making metal standards
- Deionized water
- 0.2-μm Whatman HPLC filter cartridges
- 0.2-μm nylon filters

Following are examples of preparation of IC regenerate solutions and eluents; consult the user's manual for specific compositions.

IC Regenerate Solution (0.025 N H_2SO_4). Prepare by combining 1.00 mL of concentrated H_2SO_4 with 1.00 L of deionized water. The composition of this solution will vary depending on your instrument. Consult the user's manual.

IC Eluent (1.7 mM $NaHCO_3$/1.8mM Na_2CO_3). Prepare by dissolving 1.4282 g of $NaHCO_3$ and 1.9078 g of Na_2CO_3 in 100 mL of deionized water. This 100-fold concentrated eluent solution is then diluted with 10.0 mL diluted to 1.00 L of deionized water and filtered it through a 0.2-mm Whatman nylon membrane filter, for use as the eluent. Store the concentrated solution at 4°C. Deionized water is also a reagent for washing the system after completion of the experiment. For each run, set the flow rate at 1.5 mL/min. The total cell value while running should be approximately 14 mS. Inject one or two blanks of deionized water before any standards or water samples, in order to achieve a flat baseline with a negative water peak at the beginning of the chromatogram. The composition of these solutions will vary depending on your instrument. Consult the user's manual.

IC Standards. Prepare a stock solution of the anions present in the synthetic water (chloride, nitrate, and sulfate) for each anion. For chloride, 0.208 g of NaCl should be dissolved in 100.0 mL of deionized water, yielding 1.26 g of Cl^-/L. Dilute this stock Cl^- solution 1 : 10 to give 0.126 g or 126 mg of Cl^- per litre of working standard. For nitrate, dissolve 0.155 g of $Ca(NO_3)_2$ in 100.0 mL of

deionized water to yield 1172 mg NO_3^-/L. For the sulfate stock solution, dissolve 15.113 g of $MgSO_4$ in 100.0 mL of deionized water to yield 120,600 mg of SO_4^{2-}/L. An additional 1 : 1 100 mL dilution of the sulfate stock may aid in the preparation of lower-concentration sulfate standards. Thus, the working stock solution concentrations of the anions are

- 126 ppm Cl^-
- 1172 ppm NO_3^-
- 1206 ppm SO_4^{2-}

IC standards are made from the stock solutions by dilutions using 100-mL volumetric flasks and the appropriate pipets. Each calibration level shown below contains all three anions in one 100-mL volumetric flask. Final solutions should be stored in plastic bottles to prevent deterioration of the standards.

Calibration Standard I: 0.063 ppm Cl^-, 0.565 ppm NO_3^-, and 0.603 ppm SO_4^{2-}. Make a 0.05 : 100 dilution of chloride stock and nitrate stock using a 50.0- or 100.0-μL syringe and a 100 mL volumetric flask. Make a 0.05 : 100 dilution of the 1206-ppm sulfate solution using a 50.0- or 100.0-μL syringe and fill to the 100-mL mark with deionized water.

Calibration Standard II: 0.252 ppm Cl^-, 1.13 ppm NO_3^-, and 1.21 ppm SO_4^{2-}. Make a 0.2 : 100 dilution of chloride stock using a 500.0-μL syringe, a 0.1 : 100 dilution of nitrate stock using a 250.0-μL syringe, and a 0.1 : 100 dilution of the 1206-ppm sulfate solution using a 100.0-μL syringe. Fill to the 100-mL mark with deionized water.

Calibration Standard III: 1.26 ppm Cl^-, 5.65 ppm NO_3^-, and 6.03 ppm SO_4^{2-}. Make by a 1 : 100 dilution of chloride stock, a 0.5 : 100 dilution of nitrate stock using a 500.0-μL syringe, and a 0.5:100 1206-ppm sulfate solution using a 500.0-μL syringe. Fill to the 100-mL mark with deionized water.

Calibration Standard IV: 2.52 ppm Cl^-, 11.3 ppm NO_3^-, and 12.06 ppm SO_4^{2-}. Make by a 2 : 100 dilution of chloride stock, a 1:100 dilution of nitrate stock, and a 1 : 100 dilution of the 1206-ppm sulfate solution. Fill to the 100-mL mark with deionized water.

Calibration Standard V: 5.04 ppm Cl^-, 22.6 ppm NO_3^-, and 24.12 ppm SO_4^{2-}. Make by a 4 : 100 dilution of chloride stock, a 2 : 100 dilution of nitrate stock, and a 2 : 100 dilution of the 1206-ppm sulfate solution. Fill to the 100-mL mark with deionized water.

Calibration Standard VI: 11.34 ppm Cl^-, 50.85 ppm NO_3^-, and 54.45 ppm SO_4^{2-}. Make by a 1 : 10 dilution of chloride stock, a 0.5 : 10 dilution of nitrate stock using a 500.0-μL syringe and a 0.5 : 10 dilution of the 1206-ppm sulfate solution using a 500.0-μL syringe. Fill to the 100-mL mark with deionized water.

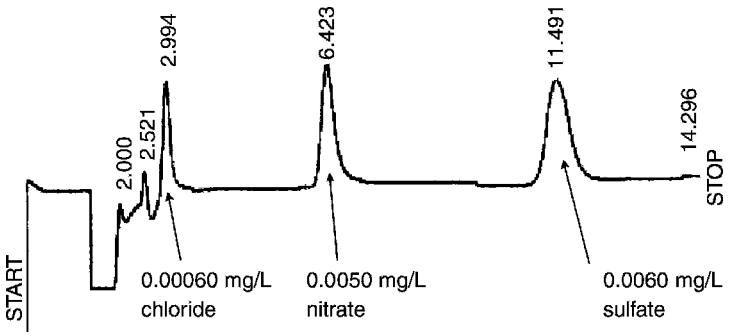

Figure 7-1. IC output for chloride, nitrate, and sulftate.

Each calibration standard solution should be filtered through a 0.45-μm Whatman HPLC filter cartridge and injected into the ion chromatograph system twice. Average peak areas should be taken based on the two injections and used to produce linear calibration graphs using the linear least squares Excel program described in Chapter 2.

To aid in your analysis, a typical ion chromatogram of chloride, nitrate, and sulfate is shown in Figure 7-1. Your retention times may differ from those shown below, but the elution order should be the same. Adjust the elution times to have a total run time of less than 15 minutes.

FAAS Standards. The cations in the synthetic water are Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}. Unlike the IC solution preparation, you must figure out how to make the calibration solutions. Stock solution concentrations should be 1000 ppm (mg/L) for each cation made from the dried and desiccated salts. Standards should be made for each cation using the approximate solution concentrations shown in the list that follows. Note that you will have to make serial dilutions of the 1000-mg/L stock solution to obtain the concentration shown below using standard class A pipets. The exact range and approximate concentrations of standards and detection limits may vary depending on the FAAS unit that you use. You may have to lower or raise the standard concentrations.

- Ca^{2+}: 1 ppm, 5 ppm, 10 ppm, 15 ppm, 20 ppm, 25 ppm, and 50 ppm
- Mg^{2+}: 0.05 ppm, 0.1 ppm, 0.2 ppm, 0.5 ppm, 1 ppm, 1.5 ppm, and 2 ppm
- Na^{+}: 0.2 ppm, 0.5 ppm, 1 ppm, 3 ppm, 5 ppm, 10 ppm, and 12 ppm
- K^{+}: 0.5 ppm, 1 ppm, 2 ppm, 3 ppm, 4 ppm, and 5 ppm

Each element will be analyzed using FAAS to create a linear calibration curve for each cation. The data can be analyzed using the linear least squares Excel sheet described in Chapter 2. You will be given a water sample by your instructor that contains each of the cations and anions mentioned above. You must determine the concentrations of each ion. Alternatively, the cations can be analyzed by IC. Consult the user's manual for specific details.

PROCEDURE

Limits of the Method. (These will vary depending on the instrument you use.)

Anions

- 0.0001 ppm Cl^-
- 0.01 ppm SO_4^{2-}
- 0.002 ppm NO_3^-

Cations

- 0.4 ppm Ca^{2+}
- 0.02 ppm Mg^{2+}
- 0.002 ppm Na^+
- 0.1 ppm K^+

This laboratory exercise will take three 4-hour laboratory periods if you are asked to perform all experiments. Alternatively, your professor may divide you into three groups: an IC group, a Ca and Mg group, and a Na and K group. If you are divided into groups, the entire exercise can be completed in one lab period, but you will be sharing your results with the remainder of the class.

IC Analysis

1. First, sign in the logbook, turn on the IC, and start the system. This will allow the eluent, column, and detector to equilibrate while you prepare your calibration standards.
2. Prepare your calibration standards as described above.
3. Dilute your water sample 1 : 500, 1 : 250, 1 : 100, and 1 : 1 for analysis, and in step 4, analyze each sample from low to high concentration until you determine the appropriate dilution to be analyzed. Analyze each water sample twice as time permits, and determine the most appropriate sample dilution based on your calibration curve (again from step 4).
4. Analyze your IC standards and then your unknown samples, making duplicate injections as time permits. Remember to record any instrument problems in the logbook as you sign out.
5. Use the linear least squares Excel program to analyze your data.

FAAS Analysis

1. First, turn on the FAAS unit and lamp. This will allow the system to warm up while you prepare your calibration standards and sample dilutions.

2. Note that all solutions/dilutions should be made in 1% HNO_3 to preserve your samples and standards.
3. Prepare your FAAS calibration standards as described earlier.
4. Dilute your water sample 1 : 500, 1 : 250, 1 : 100, and 1 : 1 and analyze each sample from low to high concentration until you determine which dilution is appropriate for analysis. Analyze each sample twice as time permits and determine the most appropriate dilution based on your calibration curve.
5. Analyze each metal separately.
6. Use the linear least squares Excel program to analyze your data.

Waste Disposal

After neutralization, all solutions can be disposed of down the drain with water.

ASSIGNMENT

Calculate the ion balance for your water sample **based on the undiluted solution**.

ADVANCED STUDY ASSIGNMENT

1. Why is the electroneutrality of a water sample important to document?
2. How do the anion and cation content affect toxicity?
3. Using your library's online search engine, find an example in the literature describing the toxicity of a complexed metal ion. The two important journals *Environmental Science and Technology* and *Environmental Toxicology and Chemistry Journal* should be included in your search.
4. Complete Table 7-2 to determine the net electroneutrality of the water sample. Is the solution balanced with respect to cations and anions?

TABLE 7-2. Calculation of the Electroneutrality of Seawater

Ion	Concentration (mg/L)	Molar Concentration (mol/L)	Charge Balance	Total Ion Balance
Cations				
Ca^{2+}	4,208			
Mg^{2+}	1,320			
Na^{+}	11,012			
K^{+}	407			
				Total cations:
Anions				
HCO_3^-	122			
Cl^-	19,780			
SO_4^{2-}	2,776			
				Total anions:
				Net difference:

Source: Based on data in Berner and Berner (1996).

8

MEASURING THE CONCENTRATION OF CHLORINATED PESTICIDES IN WATER SAMPLES

Purpose: To determine the concentration of chlorinated pesticides in a water sample

To use a capillary column gas chromatograph equipped with an electron-capture detector

BACKGROUND

Chlorinated pesticides are considered to be ubiquitous in the environment due to their refractory behavior (very slow chemical and biochemical degradation) and widespread use. For example, chemicals such as DDT and PCBs have been observed in water, soil, ocean, and sediment samples from around the world. Although the production and use of these chemicals has been banned in the United States since the 1970s, many countries (with the help of American-owned companies) continue to produce and use these chemicals on a routine basis.

Chlorinated hydrocarbons can be detected at incredibly low concentrations by a gas chromatograph detector [the electron-capture detector (ECD)] developed by James Lovelock (also the originator of the Gaia hypothesis, described in the background section of Chapter 5.) In fact, the first version of this detector was so sensitive that the company reviewing Lovelock's proposal did not believe his results and rejected his findings. Lovelock persisted and today is responsible for one of the most important and most sensitive GC detectors. The ECD can detect less than a picogram of a chlorinated compound. But with this sensitive detection

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limit comes a dilemma: How sensitive should our environmental monitoring be? Although the wisdom behind this policy is questionable, we set many exposure limits for pesticides based on how little of it we can measure with our expensive instruments. As we develop better and better instruments, we push the detection limits lower, and consequently, we set our exposure limits lower. Given the long-term presence of these compounds, we seem to be chasing a never-ending lowering of the exposure limits. Thus, we often turn to toxicology studies to determine exactly what level of exposure is acceptable.

The determination of the solubility of a specific compound is a relatively straightforward process in pure distilled water, and solubility values can be found in the literature. But how relevant are these published values to real-world samples? Literature values are available for the maximum solubility of compounds in water. In general, solubilities of hydrophobic compounds increase with temperature. But if you take a lake water sample and measure the concentration of DDT, is the DDT present only in the dissolved phase? One highly complicating factor in solubility measurements is the presence of a ''second phase'' in natural water samples that is usually described as colloidal in nature. Colloids can take the form of inorganic particles that are too small to filter from the sample or as natural organic matter (NOM) that is present in most water samples. Hydrophobic pollutants in water greatly partition to these additional particles in water and result in an apparent increase in water solubility. So if you measure the pesticide concentration of a water sample and your data indicate that you are above the water solubility, the solution may not actually be supersaturated but rather, may contain a second phase that contains additional analyte. Scientists have developed ways to detect the presence of colloid and colloid-bound pollutants, but these techniques are beyond the scope of this manual.

In this laboratory experiment you will be using a separatory funnel extraction procedure to measure the concentration of chlorinated pesticides in a water sample. This water sample is relatively pure and does not contain appreciable amounts of a second phase. This technique has been used for decades to monitor the presence of pesticides in water samples.

THEORY

If you consider only one contact time in the separatory funnel, we can define a distribution ratio, D, which describes the equilibrium analyte concentration, C_{organic}, between the methylene chloride and the water, C_{water}, phases:

$$D = \frac{[C]_{\text{methylene chloride}}}{[C]_{\text{water}}}$$

The extraction efficiency is given by

$$E = \frac{100D}{D + V_{\text{methylene chloride}}/V_{\text{water}}}$$

When D is greater than 100, which it is for most hydrophobic analytes, a single equilibrium extraction will quantitatively extract virtually all of the analyte into the methylene chloride phase. However, as you will note during the experiment, some of the methylene chloride will stick to the sides of the separatory funnel and not pass into the collection flask (a 100-mL volumetric flask). To achieve complete recovery of the methylene chloride, as well as complete extraction, you will extract the sample three times and combine the extractions in a 100-mL collection flask.

We can also estimate how many extractions are necessary to remove a specified quantity of the analyte for a series of extractions. This effectiveness can be evaluated by having an estimate of D and calculating the amount of solute remaining in the aqueous phase, $[C]_{\text{water}}$, after n extractions, where

$$[C_{\text{water}}]_n = C_{\text{water}} \left[\frac{V_{\text{water}}}{DV_{\text{organic}} + V_{\text{water}}} \right]^n$$

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Perez-Bendito, D. and S. Rubio, *Environmental Analytical Chemistry*, Elsevier, New York, 2001.

IN THE LABORATORY

Your laboratory procedure involves the extraction of very low concentrations of chlorinated pesticide/PCB in water. You will accomplish this by performing three extractions in a separatory funnel, combining these extracts, and concentrating the extract for analysis on a GC. Finally, you will analyze your samples on a capillary column GC equipped with an electron-capture detector.

Safety Precautions

- Safety glasses must be worn at all times during this laboratory experiment.
- Most, if not all of the compounds that you will use are carcinogens. Your instructor will prepare the aqueous solution of these compounds so that you will not be handling high concentrations. The purge solution you will be given contains ppb levels and is relatively safe. You should still use caution when using these solutions since the pesticides and PCBs are very volatile when placed in water. Avoid breathing the vapors from this solution.
- Most of the solvents used in this experiment are flammable. Avoid their use near open flames.

Chemicals and Solutions

Neat solutions of the following compounds will be used by your instructor to prepare the aqueous solution:

- Lindane
- Aldrin
- 2,2′,4,4′,6,6′-Hexachlorobiphenyl
- Dieldrin (not added to the solution to be extracted, but to be used as a analyte recovery check standard)
- Endosulfan I (not added to the purge solution, but to be used as a GC internal standard)

You will need, in addition:

- 80.0-ppm solution of Endosulfan I
- 80.0-ppm solution of Dieldrin
- Solid NaCl (ACS grade)
- Anhydrous Na_2SO_4 dried at 104°C

Glassware

For each student group:

- 1-L separatory funnel
- ~10 cm by ~2.0 cm drying column
- 100.0-mL volumetric flask
- Pasteur pipets
- Two 5- or 10-μL microsyringes

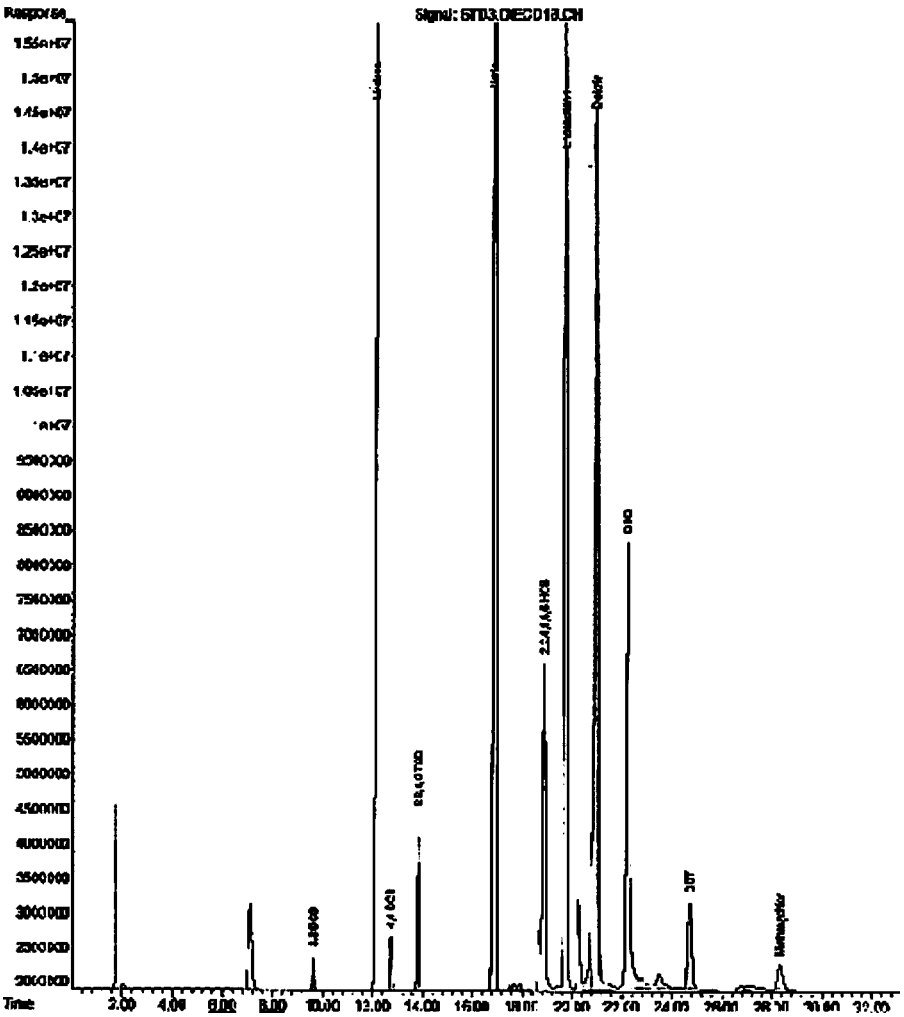

Figure 8-1. Standard chromatograph of pesticide mix on a GC–ECD (column: HP-1).